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Anomalous Photoelectric Emission from Nickel

Abstract: The photoelectric emission from a nickel ribbon has been observed as a function of temperature from 25° to 760°C, over a wavelength range from 2250 to 2530 A, qualitatively confirming and extending Cardwell's earlier work. The yield increases with temperature at all wavelengths, with an upward bulge near the Curie point. Fowler-Dubridge analyses of the emission from the front face of the ribbon, which is found to contain mainly (111) facets after extensive outgassing, yield values of the work function ranging from about 5.07 ev at 25°C to about 5.20 ev at 760°C. Behavior below the Curie point may be consistent with the magnetization-squared dependence recently suggested by Wonssowski, et al.

Introduction

This paper is a report on an investigation, briefly described earlier,[1] of the temperature dependence of the photoelectric emission from a high purity, polycrystalline nickel ribbon. The motivation of this work was twofold: (a) to make a detailed study of the anomalous change in slope in the work function/temperature characteristic near the Curie point reported by Cardwell[2] and (b) to investigate the conditions necessary for this anomaly to be detected.

First, we sought to confirm the interesting variation of photoelectric yield with temperature reported by Cardwell[2] in his similar experiments on nickel several years ago. In the intervening time, Wonssowski, Sokolow, and Wexler[3] have proposed models of both the photoelectric and thermoelectric emission from ferromagnetic metals which appear to predict, qualitatively at least, the general features of Cardwell's results. The most striking of Cardwell's results was a pronounced break in the slope of the yield-versus-temperature curves in the vicinity of the Curie temperature for each wavelength of incident light. Below that temperature, the yields increased with temperature, whereas above it they were approximately independent of temperature, or even decreased slightly, depending on wavelength.

Second, we felt that any understanding of photoemission from a ferromagnetic material would be a helpful base for an experimental investigation of the proposal by Fues and Hellmann[4] about thirty years ago, that photoelectrons emitted from ferromagnetic materials may show a net spin polarization. With the rapid development of various techniques for the measurement of electron polarization in connection with the studies of beta-decay parity, interest in experiments on photoelectron polarization has arisen.[5-7] Such polarization has not as yet been detected. However, the anomaly in the emission from nickel indicated, qualitatively at least, that some relationship might exist between the magnetic (and hence, the net electron spin orientation) and the photoelectric properties of such an emitter. Thus, it was considered that a study of the conditions necessary for this anomaly to be detected would be a significant precursor to a polarization experiment.

In this investigation, Cardwell's measurements were re-examined in the light of the Wonssowski-Sokolow-Wexler theory. In addition, several improvements over his experiments were possible: a) lower pressures were achieved during photoemission measurements, b) the temperature of the sample was measured directly to verify that any observed anomaly indeed occurred at the Curie point, and c) effects due to crystallographic orientation were at least qualitatively examined.

Experimental methods

The photoelectric cell in which these experiments were performed was similar to that used by Cardwell. As shown in Fig. 1, it consisted of a three-inch diameter Pyrex tube, mounted vertically, with feed-throughs at both ends. The top leads supported the ribbon sample and provided for the thermocouple; the bottom leads supported a cylindrical molybdenum anode which surrounded the sample. Light was admitted through a hole in the anode and a fused quartz window, which was made part of the tube envelope by means of a graded seal. A magnetically actuated shutter could be drawn over the hole in the anode to preclude evaporation of material onto the quartz window during periods of ribbon outgassing. Construction of all associated vacuum tubulation and valves was entirely of glass and metal.

In order to prevent the introduction of contaminants, the cell was initially pumped down by a liquid helium pump.[8] Thereafter, the vacuum was maintained by a 5 liter/sec "Vac-Ion" getter-ion pump. The pumping arrangement is shown in Fig. 2. The system was baked for about six hours at 450°C, after which the pressure fell to about 10^{-9} Torr. Several days later the pressure had dropped to about 10^{-10} Torr, where it remained except for transients induced by flashing of the nickel ribbon. Previous studies have demonstrated that the residual gas spectrum in such a system is appreciably more free of contaminants, such as hydrocarbon vapors, than in a comparable diffusion pumped system.[9] A Bayard-Alpert type ionization gauge (WL-5966) was used to calibrate the getter-ion pump current against pressure. The gauge was not used thereafter until the end of the experiment (to recheck the initial calibration) in order to minimize the introduction during the critical portions of the experiment of the various types of insulating contaminants detected by Bills and Evett.[10] We have previously found the ion pump current to give a reliable measure of pressure in similar systems.[11] The nickel ribbon was cut from one mil thick, vacuum melted, rolled polycrystalline foil (Nivac-P).* According to the supplier, the purity exceeded 99.9 per cent. It was cut to a width of 1/4″ except over a length of about 3/4″ at the position where the light was to impinge. Here it was

* Crucible Steel Corporation, Syracuse, New York.

Figure 1 **Experimental tube, showing nickel ribbon sample suspended from feedthroughs and surrounded by molybdenum anode.**

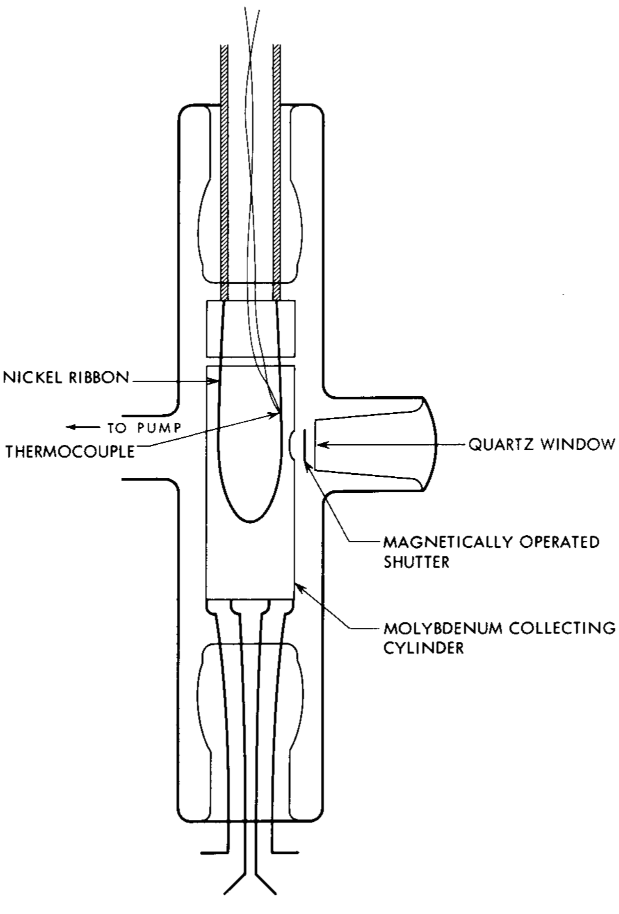
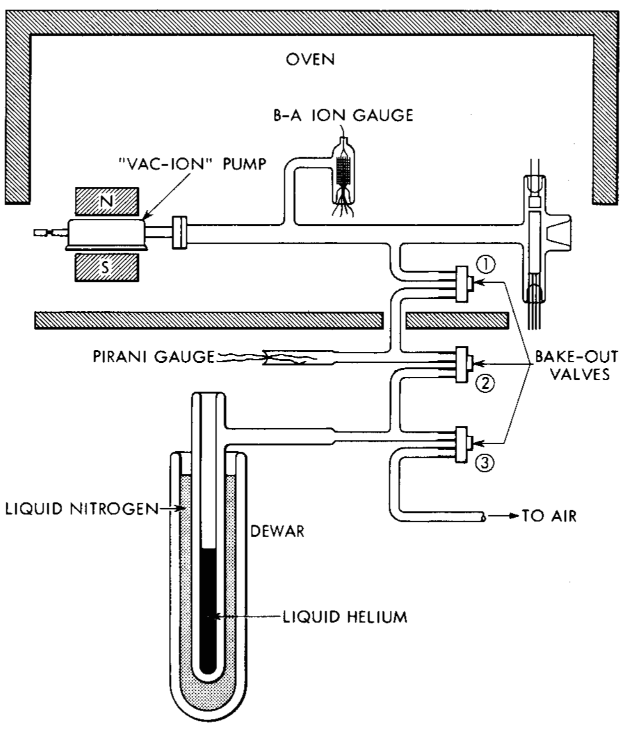


Figure 2 **Schematic diagram of ultra-high vacuum system and accessories used to attain pressure of about 10^{-10} Torr during photoemission experiments.** *Liquid helium cryogenic pump was used during initial pump-down; thereafter ion-getter (Vac-Ion) pump was used to maintain vacuum. Ion gauge was not used after ion-pump/pressure calibration was made.*



made about 20 per cent narrower in order to insure that this area, visible outside the cell, would be the hottest region during current conduction outgassing and would obviate unexpected burnout elsewhere.

The sample was electrolytically polished, carefully cleaned and then suspended from two heavy current leads at the top of the photocell. Its temperature was controlled by passing a 60 cps alternating current through it from a stabilized power supply and measured by use of both an optical pyrometer and a two-mil chromel-alumel thermocouple. The former was used for temperatures above 750°C; however, almost all measurements were at lower temperatures, making the latter the working standard. The thermocouple was spot-welded to the back of the nickel ribbon 1/4″ above the center of the illuminated region; the purpose of this separation was to prevent contamination of the nickel by diffusion of the thermocouple metals into the region of measurement. Because this location was between the center and one end of the narrow portion of the ribbon, it was anticipated, and found, that the thermocouple would indicate a temperature slightly lower than that at the illuminated (center) region. The amount of this deviation was determined by comparison with the pyrometer indications at elevated temperatures, and was found to be, for example, 35°C at 1000°C. The empirical values between 750° and 1100°C could be fitted reasonably with a straight line, which also agreed with zero deviation at room temperature. This linear dependence was used to correct thermocouple values at all temperatures. The uncertainty in observed temperature is estimated as less than 2% of the centigrade value.

As is generally the case in photoelectric experiments, extensive outgassing was required before reproducible photoelectric currents could be obtained. The nickel ribbon was kept at about 750°C for several months, with shorter periods spent at higher temperatures. Prior to, and at intervals during, photoelectric experiments, the ribbon was "flashed" to 1200°C. After the first week of pumping and such flashing, no pressure surges (over the base pressure of several times 10^{-10} Torr) were noticed whenever the sample temperature was suddenly increased from 750° to 1200°C. By the time surface stability (defined as reproducibility of photoelectric characteristics) was attained, approximately one micron of nickel had been evaporated from the surface of the sample. In addition, although the ribbon used was originally polycrystalline, this prolonged heat-treatment converted most of the region from which photoemission was obtained into oriented crystallites, indicating that some strain-anneal[12] crystal growth had taken place during the heat treatment. The crystallites were oriented mainly with their (111) faces in the plane of the ribbon.

Electron-diffraction analyses of the (111) faces of nickel crystals recently reported by Germer, Scheibner, and Hartman[13] indicate that such heat-treatment was sufficient to produce an atomically clean emitter surface. This is further corroborated by Petermann's[14] recent studies of adsorption of CO and H_2 on high-purity nickel foils. Furthermore, it is interesting to note that our work function at room temperature (5.07 ev, see below) is close to the value of 5.14 ev obtained by Madden and Farnsworth[15] for a clean (100) nickel surface. They found that to clean that surface, both heat treatment (to 1100°C) and argon ion-bombardment were required.

The optical system used for photo-excitation consisted of a super-high-pressure mercury arc lamp, grating monochromator, and calibrated detector to determine the radiant flux incident upon the sample. The lamp was a General Electric B-H6, which was operated from a stabilized supply at reduced power (about 600 instead of the rated 1000 w). This reduction increased the lamp output in the spectral region of interest in this experiment, i.e., below 2700 A. For example, at the shortest wavelengths used, in the vicinity of 2300 A, an order of magnitude increase in radiant output was attained. The Bausch and Lomb grating monochromator provided an inverse dispersion of 33 A/mm; the slits were adjusted for a triangular pass band of 10 A full width at half-maximum throughout these experiments. The wavelength settings of the instrument were checked against the lines from a low pressure mercury discharge tube.

A 1/16″ by 5/16″ image of the monochromator exit slit was formed on the nickel ribbon with a quartz-fluorite achromatic lens. The absolute intensity of this radiation was determined by slightly rotating the source and monochromator together and thereby causing the image to be formed at the plane of a photomultiplier. Previously, the absolute spectral sensitivity of a small selected portion of this tube had been determined to about ten per cent by means of an experiment involving a thermal (tungsten ribbon) lamp and calibrated monochromator.[16] Over the wavelength range of interest, the incident radiant power varied from about 1 to 10 μw. The relative radiant flux was continuously monitored during each photoelectric run by diverting a small portion of the dispersed beam into the same photomultiplier by means of a mirror.

Photoelectric currents were measured by means of a Keithley Model 410 vacuum tube electrometer. A negative bias of 22 v was applied to the nickel loop, for which the ac heating supply was isolated from ground by a transformer. This voltage was sufficient to provide saturation of the photocurrent, the magnitude of which was 10^{-14} to 10^{-12} amp.

Procedure and results

In this work, the two independent variables of direct interest were the wavelength of the incident light and the sample temperature. The photocurrent per unit incident flux (or yield in electrons per quantum) was measured as a function of one of these while the other was held fixed, yielding families of curves. Cardwell's data for nickel indicate sharp changes in the temperature dependence of the yield near the Curie temperature. In the present work, however, the yield was found to increase with temperature both below and above the Curie temperature, displaying instead an upward bulge in the vicinity of this temperature. This behavior is illustrated in Fig. 3, which shows a typical isochromatic plot of the photoelectric current as a function of sample heating current (or sample temperature).

Most of the data were taken at fixed temperatures to facilitate analysis through curve fitting by the Fowler-Dubridge (F-D) technique.[17] For each temperature, about a dozen measurements of yield were taken, each at a different wavelength. Consistent data could be taken for approximately an hour after flashing the ribbon to 1200°C. Continued occasional flashing to this temperature was necessary to accumulate a complete set of data. Measurements were taken from 25° to 760°C at wavelengths from 2250 to 2530 A.

The F-D phenomenological theory predicts that the photocurrent per unit area, for unit absorbed radiant flux density, I, is given by

$$I = \alpha A T^2 f(x) .$$

Here α is a dimensionless proportionality factor involving the probability of an electron absorbing a quantum. A is the usual electron emission constant ($\equiv 4\pi mek^2/h^3 = 120$ amp/deg^2 − cm^2), T is the absolute temperature, and f is a tabulated function of the parameter x:

$$x \equiv \frac{h\nu - \phi}{kT} ,$$

which relates radiant frequency, ν, to work function, ϕ. The quantity I is related to the experimental quantities I' (photocurrent in amperes) and n (flux in quanta/sec) by $I = I'/n$.

The results of typical measurements of emission when radiation was incident on a small portion of the front face of the sample are shown in Fig. 4. Experimental values of log (I/AT^2) have been plotted versus $h\nu/kT$ in the usual F-D manner. The curves are of the form $\log(I/AT^2) = \log \alpha + \log f(x)$. By fitting the curves to the experimental points, best values of log α and ϕ are determined; the former are gotten directly from the ordinate, the latter have been indicated (note the broken scale of the abscissa). The fit is good except near threshold for the lowest temperatures. Here the tendency to higher than corresponding F-D values may be evidence of the presence of "patches" having relatively lower work functions or higher values of α. Additionally, this deviation might indicate a small deviation from F-D theory in the case of emission from a ferromagnetic material.[18]

Similar data were also taken as illumination impinged upon the edge of the sample and hence no longer upon (111) facets. The results obtained were qualitatively similar to the foregoing, again revealing a bulge in the vicinity of the Curie temperature. The

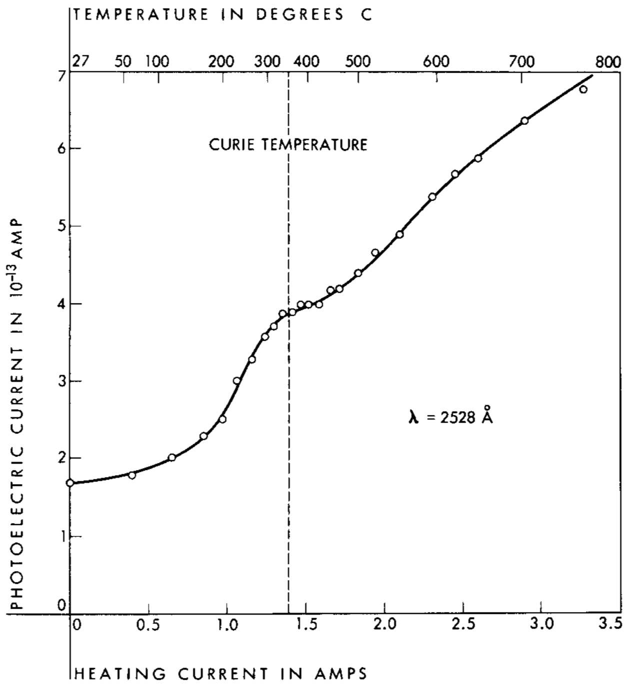
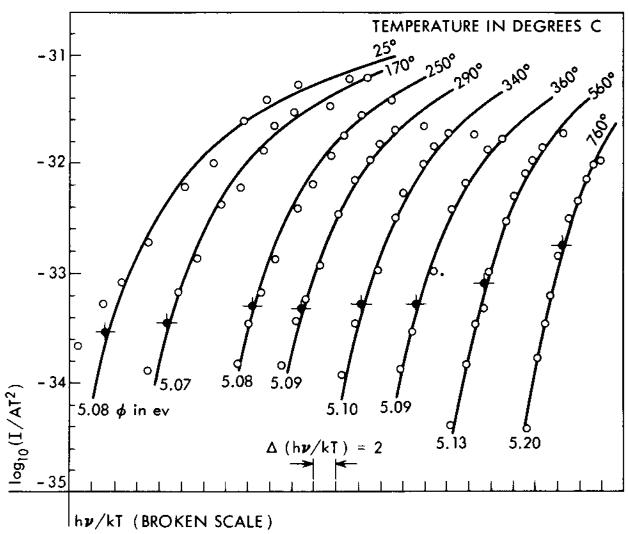


Figure 3 **Typical plot of photoelectric current versus sample heating current.** *Data taken at other wavelengths show same qualitative effect, namely a positive slope at all temperatures, with an upward bulge near the Curie point.*

Figure 4 **Fowler plots of experimental data from nickel sample at several representative temperatures.** *The ordinate is in the same absolute units for each curve, with I in units of coulombs/absorbed photon and A the usual electron emission constant. The origin of the abscissa is different for each curve but with uniform scale as shown. Best-fit theoretical curves with their origins shown by solid points have been drawn through the experimental points, and the resulting Fowler-Dubridge work functions are indicated.*



yield, however, was an order of magnitude higher, corresponding to lower values of the work function. These were lower by about 0.15 ev at room temperature and 0.25 ev at 700°C.

Interpretation

In order to determine the cause of the upward bulge in yield curves near the Curie temperature, it is instructive to plot, as a function of temperature, the values of photoelectric work function derived from the F-D analyses of the data. This has been done in Fig. 5. As indicated, there appears to be a change in slope of work function/temperature behavior in the vicinity of the Curie temperature. Cardwell's five points are included in the Figure and show striking agreement with the present experiment.

In their theory, Wonssowski, Sokolow, and Wexler assume that the photoelectrons arise predominantly from the 4*s* band. Because of an assumed exchange interaction between the 3*d* and 4*s* electrons, the 4*s* band is split into two bands having electrons of opposite spins. Below the Curie temperature, this produces perturbations in the normal temperature dependence of ϕ and α. The perturbations appear through the temperature dependence of the normalized magnetization, y, in the following manner:

$$\Delta\phi/\phi = K_1 y^2,$$

$$\Delta\alpha/\alpha = K_2 y^2.$$

The coefficients K_1 and K_2 are related to the magnitude of the assumed *s-d* interaction.

Due to uncertainties in curve-fitting of the F-D expression to the data, work function values were determined to an accuracy no better than ± 0.03 ev, thus obscuring details of the perturbation of this parameter. Hence, it was not possible to ascertain whether the effect followed a magnetization-squared dependence. Nevertheless, from the difference between the solid and the dashed (extrapolated) lines in Fig. 5, we may say that if such a dependence exists, the corresponding value of K_1, obtained by using published data on the temperature dependence of the magnetization of nickel,[19] is $+0.2$. Although the sign of K_1 is found to be positive, as predicted by the Wonssowski, Sokolow, and Wexler theory, its magnitude appears to be an order of magnitude greater than a best estimate based on semi-empirical considerations.[18]

When illumination was directed at the edge of the ribbon, a similar change in slope of the work function was observed in spite of the fact that the values themselves obtained under this condition were lower, as cited above.

Fitting of the experimental data to the F-D expression also produced values of log α. Absolute values of this parameter have been obtained through use of the calibrated light detector described in the section on experimental methods. The temperature dependence of log α for emission from the front face of the emitter is shown in Fig. 6. The reflectivity of the nickel ribbon was assumed to be independent of wavelength over the spectral region investigated here, based on measurements of Luckiesh[20] which were confirmed recently by Hass, using fresh nickel surfaces. The value of 0.40 which was obtained by Hass[21] has been used in our calculations. Cardwell demonstrated that the reflectivity is independent of temperature in the range covered here. It is seen that there is an increase in α by about a factor of five from room temperature to 760°C. Cardwell's data indicate a change by a factor of about two over the same range. Thus, it is in this parameter, not in the work function, that our results differ from those of Cardwell. The stronger increase in our value of α accounts, within the limits of applicability of the phenomenological F-D theory, for our

Figure 5 **Plot of work function derived from the Fowler analysis of Figure 4 vs temperature of the nickel sample.** *Straight-line segments have been drawn through the data points; the dashed line is an extrapolation of the high temperature values to the region below the Curie temperature.*

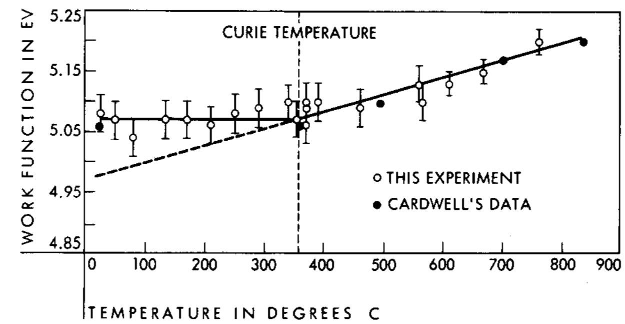
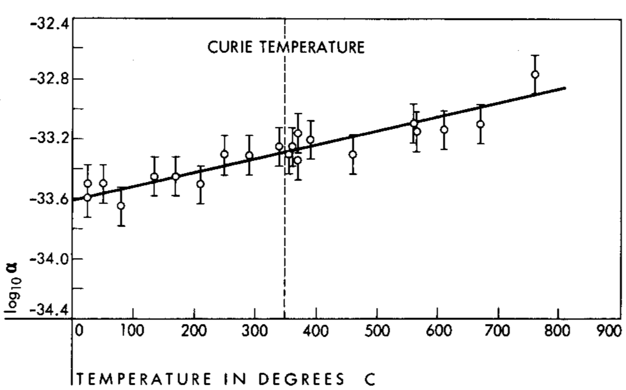


Figure 6 **Variation in the log of dimensionless probability parameter, α, as a function of temperature, as determined from Figure 4.** *Absolute values of α were obtained by using calibrated radiation detector and reflectivity data to determine the absorbed photon flux.*



relatively greater increase in yield with temperature. Uncertainties in determining α from curve-fitting to the F-D expression were too large to permit identification of a perturbation in this parameter at temperatures below the Curie temperature; i.e., no estimate is possible for the coefficient K_2.

Conclusions

It is interesting that the work function values we observed near the center of the ribbon (see Fig. 5) are in close agreement with those of Cardwell. The fact that our yield curves continue to rise above the Curie temperature is due not only to our slightly slower increase in work function with temperature, but also to increasing α. We emphasize that the work function values are those derived from a best-fit of the Fowler-Dubridge phenomenological theory, which does not explicitly involve magnetic effects. However, this parameter shows a deviation below the Curie point from extrapolated nonmagnetic values, which is not inconsistent with the magnetization-squared dependence suggested by Wonssowski, et al.

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